[Supporting Information]

Synthesis of [Os(dcbpy)$_2$(acac)]Cl (1) and [Os(dcbpy)$_2$(tfac)]Cl (2).

The precursor complex [Os(dcbpy)$_2$Cl$_2$] (**A**) (375 mg, 0.5 mmol) was dissolved in 30 mL of DMF-H_2O (2:1, v/v) in the dark under nitrogen atmosphere. Ten equivalents of each β-diketonate ligand (0.5 mL, 5.0 mmol) and sodium carbonate (Na_2CO_3) (530 mg, 5.0 mmol) were added to the solution. After stirring for 10 min at room temperature, the solution was refluxed at 140°C for 3 h. The reaction mixture was allowed to cool and the solvent was removed on a rotary evaporator. The resulting solid was dissolved in 0.1 M TBA(OH)*aq* solution, and then, this solution was washed three times with diethyl ether by using a separatory funnel. The obtained water phase solution containing the desired complex was acidified by the addition of 0.5 M HCl*aq* until the pH was 2.0 to produce a precipitate. The crude product was filtered with a membrane filter and then purified twice by column chromatography on Sephadex LH-20 using TBA(OH)*aq* solution as an eluent.

Data for [Os(dcbpy)$_2$(acac)]Cl (1). Yield 35%. Dark purple solid. ESI-MS: m/z 779.3 $[M\text{-}Cl^-]^+$. ^{1}H NMR (400 MHz, D_2O-NaOD): δ 8.89 (2H, s), 8.71 (2H, s), 8.49 (2H, d), 7.83 (2H, dd), 7.61 (2H, d), 7.20 (2H, dd), 5.63 (1H, s), 1.79 (6H, s). *Anal.* Calcd for $C_{29}H_{23}N_4O_{10}ClOs$: C, 42.83; H, 2.85; N, 6.89. Found: C, 42.59; H, 3.14; N, 6.89.

Data for [Os(dcbpy)$_2$(tfac)]Cl (2). Yield 41%. Dark purple solid. ESI-MS: m/z 829.4 $[M\text{-}Cl^-\text{-}2H^+]^-$. ^{1}H NMR (400 MHz, D_2O-NaOD): δ 8.90 (2H, sd), 8.74 (2H, sd), 8.45 (2H, d), 7.87 (2H, dd), 7.66 (2H, d), 7.25 (2H, dd), 6.08 (1H, s), 1.77 (3H, s). *Anal.* Calcd for $C_{29}H_{20}N_4O_{10}ClF_3Os+H_2O$: C, 39.35; H, 2.51; N, 6.33. Found: C, 39.27; H, 2.50; N, 6.21.

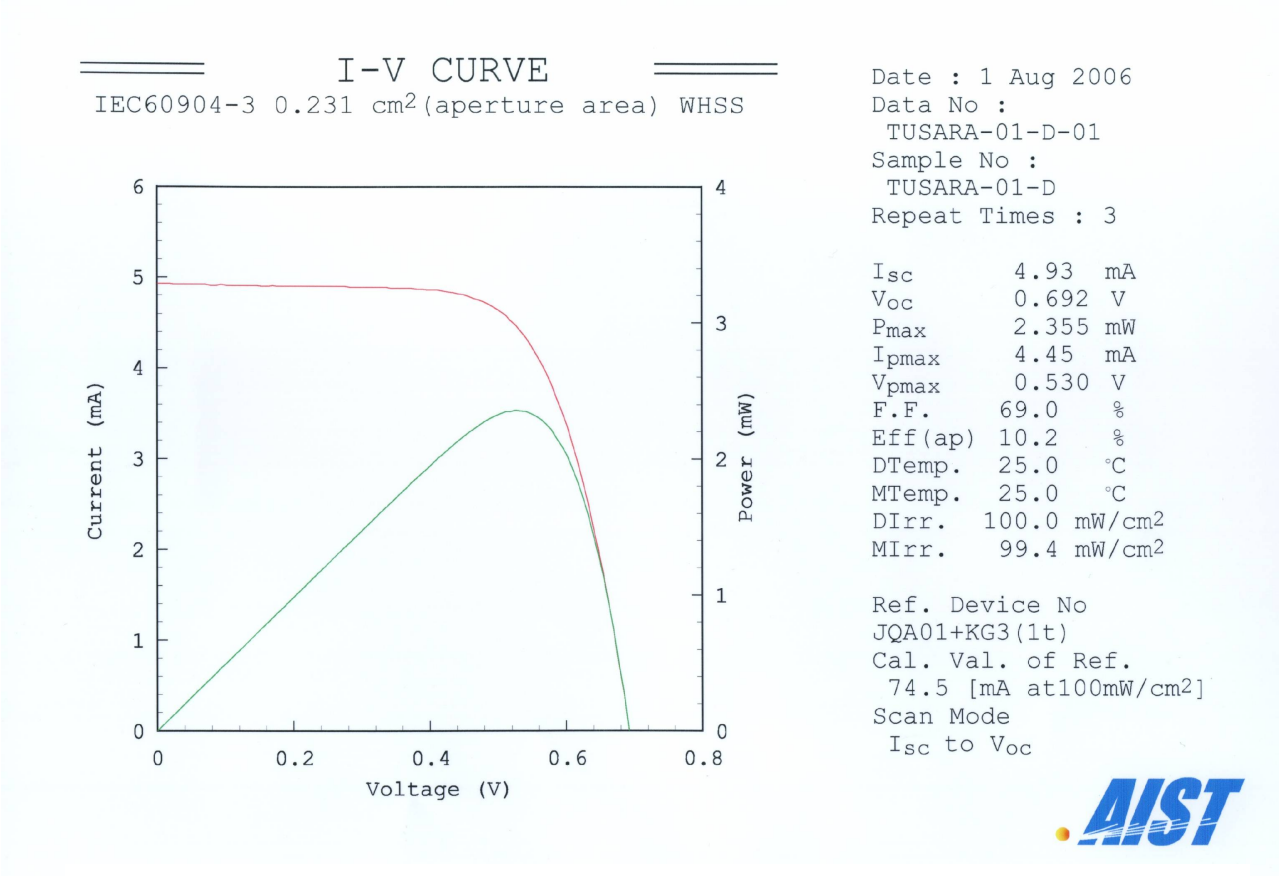

Figure S1. Solar cell performance of our optimized black-dye-sensitized solar cell measured at the RCPV, AIST, Japan.

Performance measurement of DSC at a public test centre (AIST, Japan)

The performance of our optimized **black dye** sensitized solar cell was previously measured at the RCPV, AIST, Japan. The RCPV, AIST, is an ISO/IEC 17025 certified laboratory specializing in solar cell characterization. The confirmed result was shown in **Figure S1**, which can be summarized as follows: η(ap) = 10.2%, Jsc = 21.3 mA, Voc = 0.692V, FF = 0.690 for the DSC with an area of 0.231 cm^2. In this study, we used different compositions of electrolytes and TiO_2 photoelectrodes. However, the simulated solar light calibration and cell construction were carried out in our laboratory under similar conditions of those tests.